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(21) International Application Number: PCT/US94/00028 (22) International Filing Date: 3 January 1994 (03.01.94) (30) Priority Data: 000,353 4 January 1993 (04.01.93) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventor: SINGLETON, Andy, Hugh; 453 Eastley Court, Apartment 4, Kingsport, TN 37660 (US). (74) Agent: THALLEMER, John, D.; 343 State Street, Rochester, NY 14650-2201 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIRSPRAY FORMULATIONS (57) Abstract <p>This invention relates to hair spray formulations which eliminate flaking. The hair spray formulations are based on (1) a sulfonate-containing, water-dispersible or water-dissipatable, linear polyester having a glass transition temperature of 33 °C to 60 °C, (2) a polyethylene glycol ester of a mixture of caprylic and capric acids, (3) an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms, and (4) water or a water/alcohol mixture.</p>		

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HAIR SPRAY FORMULATIONS

FIELD OF THE INVENTION

5 This invention relates to hair spray formulations which eliminate flaking. The hair spray formulations are based on (1) a sulfonate-containing, water-dispersible or water-dissipatable, linear polyester having a glass transition temperature of 33°C.
10 to 60°C., (2) a polyethylene glycol ester of a mixture of caprylic and capric acids, (3) an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms, and (4) water or a water/alcohol mixture.

15 BACKGROUND OF THE INVENTION

 Hair spray formulations typically comprise a solution of a polymer, the fixative, in water/alcohol mixtures. The polymeric materials which are typically used in hair spray formulations are soluble in water or
20 water/alcohol mixtures and are derived from N-vinylpyrrolidinone or N-vinylpyrrolidinone and one or more other vinyl monomers such as vinyl acetate, acrylate and methacrylate esters and/or styrene compounds. When applied to hair and allowed to dry, the polymeric
25 material provides human hair body, consistency, and firm texture, however, such materials have the disadvantage of flaking.

 U.S. Pat. No. 4,300,580 describes hair spray formulations containing a water-dispersible or
30 water-dissipatable linear sulfo-polyester fixative in a water/alcohol mixture. Such formulations are fast drying and have good hair holding properties but possess the disadvantage of being very difficult to remove from the hair. For example, prolonged washing is required to
35 completely remove the water-dispersible, linear polyester fixative to obtain hair with no tacky or

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sticky feel. In an effort to overcome the fixative removal problem, U.S. Pat. No. 4,300,580 teaches the addition of certain water soluble polymers to formulations containing the water-dispersible, linear polyester. The use of poly(alkylene glycols) such as poly(ethylene glycol) is disclosed. However, when such formulations containing a combination of the poly(alkylene glycol) and water-dispersible, linear polyester are applied to hair and allowed to dry, the fixative causes a matting of the hair. Such matting hinders combing, brushing and styling of hair.

U.S. Pat. No 5,030,443 discloses alginate hair setting compositions which contain an antifracking polymer agent having one or more carboxylic acid groups. The carboxylated polymers are polyacrylic and polymethacrylic acids which are used in their acid form to facilitate crosslinking.

In contrast, the present inventor has unexpectedly discovered hair spray formulations that provide human hair with body, consistency, and firm texture, without the disadvantages described hereinabove, such as flaking, tackiness, matting and difficulty in removal. The formulations of this invention may be sprayed on dry or damp hair by means of an aerosol or pump to provide a thin transparent film enhancing the natural luster of the hair without imparting a lacquered appearance thereto. The deposited film has sufficient strength to keep the hair in place, even under conditions of high humidity, but without stiffening the hair. The hair spray dries quickly to a non-tacky state which does not flake on combing but is easily removed by washing with water and mild soap or commercial shampoo preparations.

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SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide a hair spray formulation which eliminates flaking.

5 Accordingly, it is another object of the invention to provide an aerosol hair spray formulation which is not tacky, has a fast drying rate, acceptable body, consistency and firm texture necessary to hold hair in the desired arrangement for a certain length of time.

10 Still another object of the invention is to provide a hair spray formulation having excellent storage stability and which does not clog or produce foam at the exit port of an aerosol or pump container.

15 These and other objects are accomplished herein by a hair spray composition comprising:

(1) a sulfo-polyester having a Tg of 33°C. to 60°C. consisting essentially of repeat units from

20 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

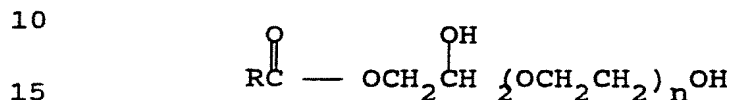
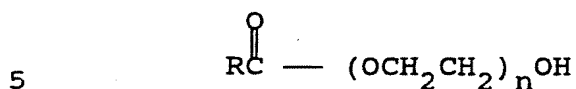
(b) a diol; and

25 (c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 4 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol;

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35 (2) a polyethylene glycol ester of a mixture of caprylic and capric acids which is selected from the group consisting of

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20 and mixtures thereof,

wherein R is $\text{CH}_3(\text{CH}_2)_n$ and n is 4 to 10;

- (3) an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms; and
- 25 (4) a liquid vehicle selected from the group consisting of water and a water/alcohol mixture.

DESCRIPTION OF THE INVENTION

30 The term "hair" as used in the present invention includes treated and untreated human hair, animal hair, and any type of fiber which requires consistency and firm texture necessary to hold it in the desired arrangement for a certain length of time.

35 The sulfo-polyester, component (1), has a glass transition temperature in the critical range of 33°C. to 60°C. and contains repeat units from a dicarboxylic acid, a diol and a difunctional sulfomonomer.

40 Dicarboxylic acids useful in the present invention include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, saturated aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, and cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Specific examples of dicarboxylic

45 acids are: terephthalic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric

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acid, adipic acid, azelaic acid, sebacic acid, and the like. The polyester may be prepared from two or more of the above dicarboxylic acids.

5 It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

10 The diol component of the polyester includes cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols are: ethylene glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 15 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 20 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. The polyester may be prepared from two or more of the above diols.

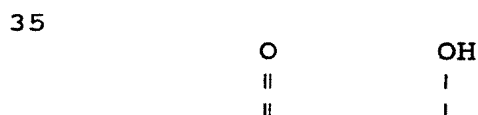
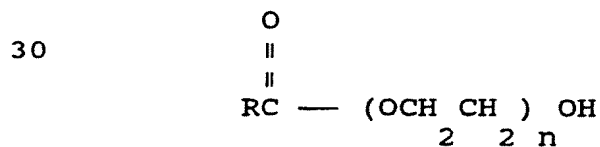
25 The difunctional sulfomonomer component of the polyester may be a dicarboxylic acid or an ester thereof containing a sulfonate group ($-\text{SO}_3^-$), a diol containing a sulfonate group, or a hydroxy acid containing a sulfonate group. The cation of the sulfonate salt may be Na^+ , Li^+ , K^+ , NH_4^+ , and 30 substituted ammonium. The term "substituted ammonium" refers to ammonium substituted with an alkyl or hydroxy alkyl radical having 1 to 4 carbon atoms. The difunctional sulfomonomer contains at least one sulfonate group attached to an aromatic nucleus wherein 35 the functional groups are hydroxy, carboxy or amino.

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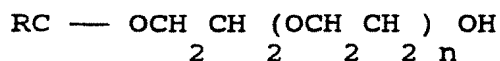
Advantageous difunctional sulfomonomer components are those wherein the sulfonate salt group is attached to an aromatic acid nucleus such as benzene, naphthalene, diphenyl, oxydiphenyl, sulfonyldiphenyl or methylenediphenyl nucleus. Preferred results are obtained through the use of sulfophthalic acid, sulfoterephthalic acid, sulfoisophthalic acid, 4-sulfonaphthalene-2,7- dicarboxylic acid, and their esters. The sulfomonomer is present in an amount from 4 to 25 mole percent, preferably 10 to 12 mole percent, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

In particularly preferred embodiments, the water dispersible sulfo-containing linear polyester is derived from a mixture of dicarboxylic acids consisting of isophthalic acid (or ester) and 5-sodio-sulfoisophthalic acid, a diol component consisting of diethylene glycol, or a mixture of diols consisting of at least 75 mole percent of diethylene glycol with the remaining diol being either ethylene glycol or 1,4-cyclohexane-dimethanol. The sulfo-polyester, component (1), is present in an amount of 1 to 10 weight percent, based on the weights of components (1), (2), (3) and (4) of the hair spray formulation.

Component (2) of the hair spray is a polyethylene glycol ester of a mixture of caprylic and capric acids which is selected from the group consisting of



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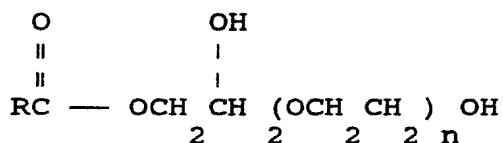


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and mixtures thereof wherein R is $\text{CH}_3(\text{CH}_2)_n$ and n is 4 to 10. Suitable examples include polyethylene glycol 400 monocaprate, polyethylene glycol 400 monocaprylate, polyethylene glycol 400 caprylate/caprate and polyethylene glycol 300 caprylic/capric glycerides. A preferred polyethylene glycol ester of a mixture of caprylic and capric acids is

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wherein RCO is a mixture of caprylic and capric radicals and n has an average value of 6.

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Component (3) of the hair spray is an alpha-hydroxy carboxylic acid which has 2 to 6 carbon atoms. A preferred alpha-hydroxy carboxylic acid is lactic acid. The alpha-hydroxy carboxylic acid may be added in neat form or in solution with water, such as a 50/50 acid/water weight percent solution.

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Component (4) of the hair spray is a liquid vehicle. The liquid vehicle of the formulations may be water or a water/alcohol mixture. Distilled or deionized water are the preferred sources of water since tap water generally contains ions which would precipitate the sulfopolyester, component (1). The alcohol should have two to four carbon atoms. Specific alcohols include, ethanol, isopropanol and t-butanol.

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The present inventor has determined that for aerosol hair sprays, the liquid vehicle is preferably water. However, a water/alcohol mixture may be employed as long as the alcohol is present in an amount less than 50 weight percent. In such aerosol hair spray formulations where an alcohol/water mixture is employed, preferably 35 to 45 weight percent of the mixture is alcohol. In pump formulations, the liquid vehicle may consist of up to 80 weight percent alcohol. The preferred alcohol is ethanol. The liquid vehicle is present in an amount of 46 to 94 weight percent, based on the weights of components (1), (2), (3) and (4) of the hair spray formulation. Preferably, the liquid vehicle is present in an amount of 55 to 70 weight percent, based on the weights of components (1), (2), (3) and (4) of the hair spray formulation.

For aerosol hair spray formulations, a propellant selected from the group consisting of a $C_1 - C_4$ aliphatic hydrocarbons and dimethyl ether, is necessary. The aliphatic hydrocarbons may be branched or straight chain and include methane, ethane, propane, n-butane, isobutane, or mixtures thereof. A preferred aliphatic hydrocarbon propellant is a mixture containing 83 percent isobutane and 17 percent propane. The propellant is present in an amount of 3 to 40 weight percent, based on the weights of components (1), (2), (3) and (4) of the aerosol hair spray formulation. In the case where a $C_1 - C_4$ aliphatic hydrocarbon is used as the propellant, generally 3 to 10 weight percent, preferably 4 to 7 weight percent, is employed. In the case where dimethyl ether is used as the propellant, generally, 30 to 40 weight percent, preferably, 30 to 35 weight percent, is employed.

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Other conventional additives such as preservatives, fragrances, antifoaming agents, hair conditioners, plasticizers, etc. may be added in such quantities as desired, up to 5.0% by weight of the total formulation.

5 Although the film-forming formulations described herein are particularly useful as aerosol hair sprays for the grooming of hair, it is possible that the formulations, with or without modification, may be used in other types of personal care products.

10 The materials and testing procedures used for the results shown herein are as follows:

DYMEL A (trademark) (CTFA Adopted Name: Dimethyl Ether) available from DuPont, is a dimethyl ether.

15 FINSOLV PL-355 (trademark) is available from Finetex, is an alkoxylated alcohol ester.

DOW CORNING 190 (trademark) (CTFA Adopted Name: Dimethicone Copolyol) available from Dow Corning, is a polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene side chains.

20 SOFTIGEN 767 (trademark) is available from Hüls, is a polyethylene glycol caprylic/capric monoglyceride.

Inherent viscosity (I.V.) was measured at 23°C. using 0.50 grams of polymer per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

25 Preparation of tresses involved natural brown, European virgin hair. About two grams of hair, root end, were glued to a 2" by 2" (5 cm by 5 cm) plastic tab. The tresses were cut so that the length of hair hanging below the tabs was six inches (15.2 cm).

30 Preparation of the 28% dispersions of water-dispersible sulfo-polyester:

A. Sulfo-Polyester A was prepared as follows: A 500 mL round bottom flask equipped with a ground-glass head, an agitator shaft, nitrogen inlet and a side arm

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was charged with 74.0 grams of isophthalic acid, 16.0 grams of 5-sodiosulfoisophthalic acid, 106.0 grams of diethylene glycol, sufficient titanium isopropoxide to provide 50 ppm of titanium, and 0.45 grams of sodium acetate tetrahydrate. The flask was immersed in a Belmont bath at 200°C. for two hours under a nitrogen sweep. The temperature of the bath was increased to 280°C. and the flask was heated for one hour under reduced pressure of 0.5 to 0.1 mm of Hg. The flask was allowed to cool to room temperature and the copolyester was removed from the flask. The copolyester had an I.V. of 0.45 and a glass transition temperature of 30°C. as measured using a differential scanning calorimeter (DSC). The copolyester was extruded and pelletized.

A 28% solids dispersion of Sulfo-Polyester A in water was prepared by heating the water to a temperature of 75°C. to 85°C. and adding the required amount of pellets while agitating at a rate sufficient to maintain the pellets in suspension. The heating was continued until all the pellets were dispersed, approximately, 20 to 30 minutes. Water was added to replace evaporation loss. The dispersion was cooled and filtered.

B. Sulfo-Polyester B was prepared as follows: A 500 mL round bottom flask equipped with a ground-glass head, an agitator shaft, nitrogen inlet and a side arm was charged with 74.0 grams of isophthalic acid, 16.0 grams of 5-sodiosulfoisophthalic acid, 83.0 grams of diethylene glycol, 16.0 grams of 1,4-cyclohexane-dimethanol, sufficient titanium isopropoxide to provide 50 ppm of titanium, and 0.45 grams of sodium acetate tetrahydrate. The flask was immersed in a Belmont bath at 200°C. for one hour under a nitrogen sweep. The temperature of the bath was increased to 230°C. for one hour. The temperature of the bath was increased to 280°C. and the flask was heated for 45 minutes under

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reduced pressure of 0.5 to 0.1 mm of Hg. The flask was allowed to cool to room temperature and the copolyester was removed from the flask. The copolyester had an I.V. of 0.36 and a glass transition temperature of 38°C. as measured using a differential scanning calorimeter (DSC). The copolyester was extruded and pelletized.

A 28% solids dispersion of Sulfo-Polyester B in water was prepared by heating the water to a temperature of 90°C. to 95°C. and adding the required amount of pellets while agitating at a rate sufficient to maintain the pellets in suspension. The heating was continued until all the pellets were dispersed, approximately, 20 to 30 minutes. Water was added to replace evaporation loss. The dispersion was cooled and filtered.

C. Sulfo-Polyester C was prepared as follows: A 500 mL round bottom flask equipped with a ground-glass head, an agitator shaft, nitrogen inlet and a side arm was charged with 136.0 grams of isophthalic acid, 53.0 grams of 5-sodiosulfoisophthalic acid, 155.0 grams of diethylene glycol, 78.0 grams of 1,4-cyclohexane-dimethanol, sufficient titanium isopropoxide to provide 50 ppm of titanium, and 1.48 grams of sodium acetate tetrahydrate. The flask was immersed in a Belmont bath at 200°C. for one hour under a nitrogen sweep. The temperature of the bath was increased to 230°C. for one hour. The temperature of the bath was increased to 280°C. and the flask was heated for 45 minutes under reduced pressure of 0.5 to 0.1 mm of Hg. The flask was allowed to cool to room temperature and the copolyester was removed from the flask. The copolyester had an I.V. of 0.33 and a glass transition temperature of 55°C. as measured using a differential scanning

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calorimeter (DSC). The copolyester was extruded and pelletized.

5 A 28% solids dispersion of Sulfo-Polyester C in water was prepared by heating the water to a temperature of 85°C. to 90°C. and adding the required amount of pellets while agitating at a rate sufficient to maintain the pellets in suspension. The heating was continued until all the pellets were dispersed, approximately, 20 to 30 minutes. Water was added to replace evaporation loss. The dispersion was cooled and filtered.

10 The invention will be further illustrated by a consideration of the following examples, which are intended to be exemplary of the invention. All parts and percentages in the examples are on a weight basis unless otherwise stated.

EXAMPLE I

Hair spray was prepared according to the following formulation:

20	<u>Ingredient</u>	<u>Weight %</u>
	Distilled Water	57.97
	HYDROTRITICUM WAA (trademark)	0.20
	28% Dispersion of Sulfo-Polyester A	40.83
	SOFTIGEN 767	1.00

25 This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester A, and SOFTIGEN 767 to the water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. The hair treated with the aerosol hair spray had a tacky or sticky feel.

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EXAMPLE II

Hair spray was prepared according to the following formulation:

	<u>Ingredient</u>	<u>Weight %</u>
5	Distilled Water	57.97
	HYDROTRITICUM WAA	0.20
	28% Dispersion of Sulfo-Polyester B	40.83
	SOFTIGEN 767	1.00

10 This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester A, and SOFTIGEN 767 to the water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl
15 ether was prepared. The aqueous aerosol formulation showed good clarity and storage stability for a period of at least 3 months. The formulation was applied in the form of an aerosol hair spray to hair tresses. A minor amount of flaking was observed after drying and
20 brushing the tresses.

EXAMPLE III

Hair spray was prepared according to the following formulation:

25	<u>Ingredient</u>	<u>Weight %</u>
	Distilled Water	56.47
	HYDROTRITICUM WAA	0.20
	28% Dispersion of Sulfo-Polyester B	40.83
	50% Solution of Lactic Acid	2.00
30	50% Solution of Sodium Hydroxide	0.50

This hair spray formulation was prepared by adding sodium hydroxide to the lactic acid such that the pH was 4.0 to 5.5. The solution was then combined with water.
35 HYDROTRITICUM WAA and the 28% dispersion of Sulfo-

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Polyester B were added to the water solution and mixed until well dispersed. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE IV

Hair spray was prepared according to the following formulation:

	Ingredient	Weight %
	Distilled Water	55.47
	50% Solution of Lactic Acid	2.00
	50% Solution of Sodium Hydroxide	0.50
15	HYDROTRITICUM WAA	0.20
	28% Dispersion of Sulfo-Polyester B	40.83
	SOFTIGEN 767	1.00

This hair spray formulation was prepared by adding sodium hydroxide to the lactic acid such that the pH was 4.0 to 5.5. The solution was then combined with water. HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester B, and SOFTIGEN 767 were added to the water solution and mixed until well dispersed. The hair spray formulation was applied to hair tresses by means of a pump. No flaking was observed after drying and brushing the tresses. In addition, the hair spray formulation provided the hair with good hold properties without a tacky or sticky feel.

EXAMPLE V

A 70/30 ratio of the hair spray prepared in Example III to dimethyl ether was prepared. The aqueous aerosol formulation showed good clarity and storage stability for a period of at least 3 months. The

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formulation was applied in the form of an aerosol hair spray to hair tresses. No flaking was observed after drying and brushing the tresses. In addition, the hair spray formulation provided the hair with good hold properties without a tacky or sticky feel.

EXAMPLE VI

A 70/30 ratio of the hair spray prepared in Example III to a mixture containing 83 percent isobutane and 17 percent propane was prepared. The aqueous aerosol formulation showed good clarity and storage stability for a period of at least 3 months. The formulation was applied in the form of an aerosol hair spray to hair tresses. No flaking was observed after drying and brushing the tresses. In addition, the hair spray formulation provided the hair with good hold properties without a tacky or sticky feel.

EXAMPLE VII

Hair spray was prepared according to the following formulation:

	Ingredient	Weight %
	Distilled Water	55.47
	50% Solution of Lactic Acid	2.00
25	50% Solution of Sodium Hydroxide	0.50
	HYDROTRITICUM WAA	0.20
	28% Dispersion of Sulfo-Polyester C	40.83
	SOFTIGEN 767	1.00

This hair spray formulation was prepared by adding sodium hydroxide to the lactic acid such that the pH was 4.0 to 5.5. The solution was then combined with water. HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester C, and SOFTIGEN 767 were added to the water solution and mixed until well dispersed. The hair spray

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formulation was applied to hair tresses by means of a pump. No flaking was observed after drying and brushing the tresses. In addition, the hair spray formulation provided the hair with good hold properties without a tacky or sticky feel.

EXAMPLE VIII

Hair spray was prepared according to the following formulation:

Ingredient	Weight %
Distilled Water	56.97
HYDROTRITICUM WAA	0.20
28% Dispersion of Sulfo-Polyester B	40.83
Glycerol Diacetate	2.00

This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester B, glycerol diacetate, water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE IX

Hair spray was prepared according to the following formulation:

Ingredient	Weight %
Distilled Water	56.97
HYDROTRITICUM WAA	0.20
28% Dispersion of Sulfo-Polyester B	40.83
Glycol Monoacetate	2.00

This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-

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Polyester B, glycol monoacetate, water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE X

Hair spray was prepared according to the following formulation:

Ingredient	Weight %
Distilled Water	34.97
HYDROTRITICUM WAA	0.20
28% Dispersion of Sulfo-Polyester B	40.83
Propylene Glycol	24.00

This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester B, propylene glycol, water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE XI

Hair spray was prepared according to the following formulation:

Ingredient	Weight %
Distilled Water	58.96
HYDROTRITICUM WAA	0.20
28% Dispersion of Sulfo-Polyester B	40.83
Dow Corning 190 Surfactant	0.01

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This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester B, Dow Corning 190 Surfactant, water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE XII

A hair spray was prepared according to Example XI except that the Dow Corning 190 Surfactant was increased to 0.05 weight percent. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The all aqueous aerosol formulation showed good clarity and storage stability. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed while drying and brushing the tresses.

EXAMPLE XIII

Hair spray was prepared according to the following formulation:

	Ingredient	Weight %
25	Distilled Water	58.67
	HYDROTRITICUM WAA	0.20
	28% Dispersion of Sulfo-Polyester B	40.83
	FINSOLVE 355	0.30

This hair spray formulation was prepared by adding the HYDROTRITICUM WAA, the 28% dispersion of Sulfo-Polyester B, FINSOLVE 355, water and mixing until well dispersed. The pH was determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an

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aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

EXAMPLE XIV

5 Hair spray was prepared according to the following formulation:

	<u>Ingredient</u>	<u>Weight %</u>
	Distilled Water	58.67
	28% dispersion of Sulfo-Polyester B	40.83
10	FINSOLVE 355	0.50

This hair spray formulation was prepared by adding the 28% dispersion of Sulfo-Polyester B, FINSOLVE 355, water and mixing until well dispersed. The pH was
15 determined to be 5.0 to 5.5. A 70/30 ratio of the hair spray to dimethyl ether was prepared. The formulation was applied in the form of an aerosol hair spray to hair tresses. Flaking was observed after drying and brushing the tresses.

20 Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious modifications are within the full intended scope of the appended claims.

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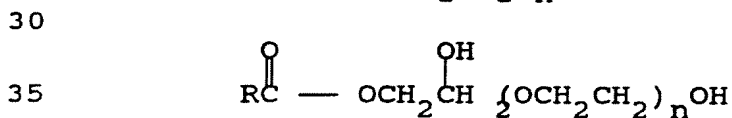
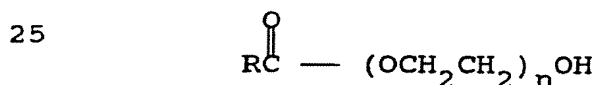
WHAT IS CLAIMED IS:

1. A hair spray formulation comprising:

(1) a sulfo-polyester having a Tg of 33°C. to 60°C. consisting essentially of repeat units from

- 5 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;
- 10 (b) a diol; and
- (c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino,
- 15 provided the difunctional sulfomonomer is present in an amount from 4 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol;

20 (2) a polyethylene glycol ester of a mixture of caprylic and capric acids which is selected from the group consisting of



40 and mixtures thereof,

wherein R is $\text{CH}_3(\text{CH}_2)_n$ and n is 4 to 10;

- (3) an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms; and
- 45 (4) a liquid vehicle selected from the group consisting of water and a water/alcohol mixture.

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2. A hair spray formulation comprising:

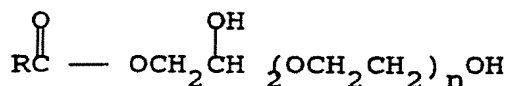
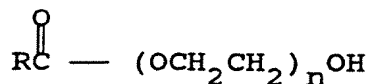
(1) 1 to 10 weight percent based on the weight of components (1), (2), (3) and (4) of a sulfo-polyester having a Tg of 33°C. to 60°C. consisting essentially of repeat units from

(a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

(b) a diol; and

(c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 4 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

(2) 0.5 to 5.0 weight percent of a polyethylene glycol ester of a mixture of caprylic and capric acids which is selected from the group consisting of



and mixtures thereof,

wherein R is $\text{CH}_3(\text{CH}_2)_n$ and n is 4 to 10;

(3) 0.5 to 5.0 weight percent of an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms; and

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(4) 46 to 94 weight percent of a liquid vehicle selected from the group consisting of water and a water/alcohol mixture.

5 3. A hair spray formulation comprising:

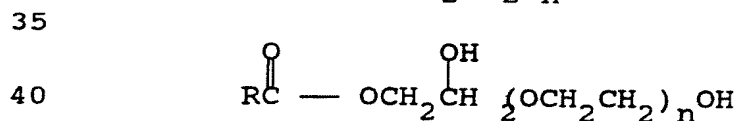
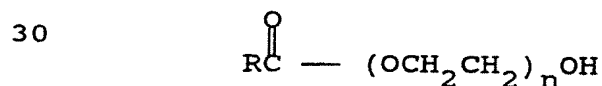
(1) 3 to 7 weight percent based on the weight of components (1), (2), (3) and (4) of a sulfo-polyester having a glass transition temperature of 33°C. to 60°C. consisting essentially of repeat units from

10 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

15 (b) a diol; and

(c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 4 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

25 (2) 1 to 3 weight percent of a polyethylene glycol ester of a mixture of caprylic and capric acids which is selected from the group consisting of



45 and mixtures thereof,
wherein R is $\text{CH}_3(\text{CH}_2)_n$ and n is 4 to 10;

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(3) 1 to 3 weight percent of an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms; and

(4) 55 to 70 weight percent of a liquid vehicle selected from the group consisting of water and a water/alcohol mixture.

4. The hair spray formulation of Claim 1 wherein the dicarboxylic acid component is selected from the group consisting of terephthalic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, and mixtures thereof.

5. The hair spray formulation of Claim 4 wherein the dicarboxylic acid component is isophthalic acid.

6. The hair spray formulation of Claim 1 wherein the diol component is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, and mixtures thereof.

7. The hair spray formulation of Claim 6 wherein the diol component is a mixture of diethylene glycol and 1,4-cyclohexanedimethanol.

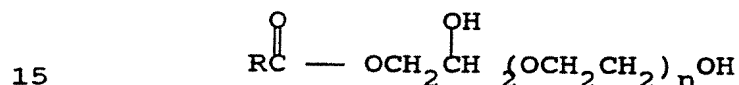
8. The hair spray formulation of Claim 1 wherein the difunctional sulfomonomer component is selected from the group consisting of sulfophthalic acid, sulfoterephthalic acid, sulfoisophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, and esters thereof.

9. The hair spray formulation of Claim 8 wherein the difunctional sulfomonomer component is 5-sodio-sulfoisophthalic acid.

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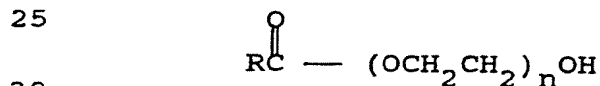
10. The hair spray formulation of Claim 1 wherein the sulfo-polyester, component (1), has repeat units from isophthalic acid, diethylene glycol and 1,4-cyclohexanedimethanol, and 5-sodio-sulfoisophthalic acid.

11. The hair spray formulation of Claim 1 wherein the polyethylene glycol ester of a mixture of caprylic and capric acids, component (2), is



wherein RCO is a mixture of caprylic and capric radicals and n has an average value of 6.

12. The hair spray formulation of Claim 1 wherein the polyethylene glycol ester of a mixture of caprylic and capric acids, component (2), is



wherein RCO is a mixture of caprylic and capric radicals and n has an average value of 8.

13. The hair spray formulation of Claim 1 wherein the alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms, component (3), is lactic acid.

14. The hair spray formulation of Claim 1 wherein the alcohol component of the water/alcohol mixture, component (4), is selected from the group consisting of ethanol, isopropanol, t-butanol and mixtures thereof.

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15. The hair spray formulation of Claim 1 which additionally contains 3 to 40 weight percent based on the weight of components (1), (2), (3), and (4) of a propellant selected from the group consisting of a
5 C₁ - C₄ aliphatic hydrocarbon, dimethyl ether, and mixtures thereof.
16. The hair spray formulation of Claim 15 wherein the dimethyl ether propellant is present in an amount of
10 30 to 40 weight percent based on the weight of components (1), (2), (3), and (4).
17. The hair spray formulation of Claim 15 wherein the C₁ - C₄ aliphatic hydrocarbon propellant is selected
15 from the group consisting of methane, ethane, propane, n-butane, isobutane, and mixtures thereof.
18. The hair spray formulation of Claim 17 wherein the propellant is a mixture containing 83 weight percent
20 isobutane and 17 weight percent propane.
19. The hair spray formulation of Claim 1 which additionally contains an additive selected from the group consisting of preservatives, fragrances,
25 antifoaming agents, hair conditioners and plasticizers.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/00028

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A61K7/06 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 158 762 (PIERCE) 27 October 1992 see the whole document ---	1-19
A,P	WO,A,93 01797 (L'OREAL) 4 February 1993 see page 7, line 30 - line 31 -----	1-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

14 March 1994

Date of mailing of the international search report

28.03.1994

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US 94/00028

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5158762	27-10-92	WO-A- 9317658	16-09-93
WO-A-9301797	04-02-93	FR-A- 2679444	29-01-93
		CA-A- 2090864	26-01-93
		EP-A- 0550745	14-07-93